Removal of Perchlorate in Biologically Active Carbon Adsorption Systems[a]

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Introduction

In April 1997, the limit of detection for perchlorate (ClO_4^-) decreased from 400 µg/L to 4 µg/L[1]. Since that time, perchlorate concentrations ranging from single digits to hundreds of µg/L have been found in drinking water supplies in California, Nevada, and Arizona. Ammonium perchlorate is an oxidizer which helps rocket fuel ignite and burn, and it is often a component of munitions. Since ammonium perchlorate has a limited shelf life, it is frequently washed out of the nation's solid rocket supply. Contamination is likely the result of the large volumes of perchlorate-containing water generated during this process. Perchlorate contamination could also be due to wastes produced by the munitions industry or from areas subjected to substantial use of explosives, such as mines. Only six states in the U.S. do not contain users or manufacturers of perchlorate.[2]

Perchlorate has the ability to disrupt the thyroid gland's use of iodine in the generation of metabolic hormones. No state or federal standard for perchlorate currently exists in the U.S. since perchlorate contamination has only recently come to the forefront. However, based on a 1992 health study conducted by the U.S. Environmental Protection Agency (USEPA), the California Department of Health Services established a provisional perchlorate action level of 18 µg/L. The USEPA recently amended the recommended reference dose to 0.009 mg/kg-day for a 70 kg person drinking 2 liters of water per day which results in an action level of 32 µg/L[2].

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[a] **Note:** This abstract is not distinct from those found in the proceedings for the 1999 AWWA conference and the 1999 Water Quality and Technology Conference.

The occurrence of perchlorate in drinking water supplies has not been well established. The state of California has shut down 18 wells due to perchlorate contamination up to 280 μg/L[1]. More complete data will be collected in a survey funded by AWWARF that targets both surface and groundwater supplies in the United States.

Biological and chemical reduction processes, membrane processes, and ion exchange are being investigated for perchlorate removal. This project briefly examines perchlorate removal via ion exchange and chemical reduction. The focus of this research, however, is the biological reduction of perchlorate. Reduction processes are based on the fact that perchlorate is thermodynamically unstable. According to free energy relationships, perchlorate can oxidize water to form oxygen, resulting in the following overall reaction (Note: H_2O appears in the oxygen half-reaction but not the overall reaction):

$$ClO_4^- \Rightarrow Cl^- + 2\ O_2$$

This reaction has a large energy barrier that keeps it from taking place in the absence of a catalyst. Similar to free and combined chlorine, chlorite, chlorate, and bromate, the low concentrations of perchlorate in drinking water are kinetically stable. An objective of this research is to find a microbe with the right enzyme, or a catalytic solid, that can enable this reaction to proceed rapidly.

In a study of biological reduction, Rikken et al.[3] found that a microorganism in the - subgroup of the *Proteobacteria* was able to use perchlorate as an electron acceptor. Hurley et al.[4] describe a pilot system that is in place at Tyndall Air Force base to treat the wash water from motors containing ammonium perchlorate. In this system, *Wolinella succinogenes* is the bacterial species that is able to reduce perchlorate to chloride. Hurley et al.[4] note perchlorate reduction from 3000 mg/L to 0.5 mg/L. Biological reduction of perchlorate in the μg/L concentration range has only recently been achieved. At a recent perchlorate conference (Ontario, CA, March 18-19, 1999), work done in the labs of Dr. William Frankenberger, Jr. and Dr. Bruce Logan was presented describing the biological reduction of perchlorate at low μg/L concentrations. Dr. Frankenberger et al. used a pure culture of *Perclace* to reduce perchlorate to below detection using sand filters with acetate serving as the electron donor.[5] Dr. Logan et al. isolated perchlorate-reducing microorganisms from a sample of local wastewater and utilized these microorganisms in various bioreactor configurations to achieve reduction of perchlorate.[6]

Biologically active carbon (BAC) is a potentially promising application of activated carbon for perchlorate removal from natural water. Carbon is rendered biologically active by contacting the carbon extensively with natural water. Microorganisms present in the water can colonize the GAC.[7] They can use the biodegradable fraction of NOM as an electron donor. An externally added electron donor solution could also be added. Dissolved oxygen (DO) and nitrate (NO_3^-) are common microbial electron acceptors, although perchlorate can also be used as an electron acceptor. Therefore, it is possible that perchlorate could be reduced to chloride if it is used as a microbial electron acceptor.

Objectives

There were three primary objectives of this research project:

(1) To establish the ion-exchange capacity of Norit GAC for perchlorate.

(2) To establish that perchlorate at low μg/L concentrations can be biologically removed to below the limit of detection (2.0 μg/L) using BAC filtration.

(3) To determine a correlation between nitrate concentration and level of perchlorate removal.

Materials and Methods

Granular Activated Carbon. The carbon used in this study was Norit RO 0.8, lot number 72303-5 (Norit Americas Inc., Atlanta, Georgia). Norit carbon is an extruded peat activated by steam. It has an average particle diameter of 0.8 mm and surface area of 907 m^2/g.

Biologically Active Carbon. BAC was formed by extensive preloading of the carbon with dechlorinated Champaign-Urbana tapwater (CUW) that was spiked with 50 μg/L perchlorate and 20 μg/L bromate. The columns were operated at a 25 minute empty bed contact time for 600 bed volumes. At the end of this preloading period, approximately 60% of the influent DOC and 90% of the influent bromate were consistently being removed by the microorganisms. Therefore, by the end of the preloading periods, the filters were considered biologically active.

Biologically active carbon filters were constructed in one inch diameter glass pipes (Ace Glass, Vineland, New Jersey). The pipes were capped with teflon endcaps. A small layer of 3 mm glass beads was placed above and below the carbon bed in order to promote uniform flow characteristics and prevent channeling. For this study, two BAC filter apparatuses were constructed. Each apparatus consisted of an influent reservoir and two BAC filters in series. Influent was pumped through the columns using peristaltic Masterflex pumps (Cole-Parmer, Vernon Hills, Illinois). Each influent reservoir was fitted with a floating cover, made of stainless steel, to prevent diffusion of oxygen into the influent for low dissolved oxygen experiments.

Influent Water. Once the filters were rendered biologically active, the base water for the influent to one set of columns was switched from CUW to deionized, distilled water (DDW). This allowed for better control over influent conditions. The typical dissolved organic carbon (DOC) concentration of DDW is approximately 0.15 mg/L. The base water for the influent to the other set of columns remained as CUW. The typical DOC concentration of CU water is approximately 1.5 mg/L. The desired components of the various influent matrices were spiked into the influent water.

Perchlorate. Reagent grade sodium perchlorate (Sigma Chemical Co., St. Louis, Missouri) was dried overnight in a 105 °C oven and subsequently stored in a desiccator.

Electron Donor Solution. Due to the fact that perchlorate reduction was not achieved in either apparatus through 6200 BV of flow, an electron donor solution was applied externally just before the influent reached the first BAC bed. The donor solution was a mixture of acetate, lactate, and pyruvate (all reagent grade Sigma Chemical Co., St. Louis, Missouri) at a concentration of 2.0 mg/L as carbon and 5.0 mg/L as O_2. The donor was added using a syringe pump (kd Scientific).

Dissolved Oxygen Concentration. Dissolved oxygen (DO) concentration was maintained at 2.5 mg/L throughout this study. Low DO concentrations were achieved by stripping the oxygen from the water with lab-grade nitrogen gas.

Bromate, Nitrite, Nitrate Analyses. Bromate, nitrite and nitrate were analyzed by ion chromatography. The ion chromatography system consisted of a Dionex Series 300 ion chromatograph (Sunnyvale, California) with an anion self-regenerating suppressor (ASRS-1) and conductivity meter. The columns used were Dionex ionpac NG1, AG9-HC, and AS9-HC; the purpose of the NG1 was to absorb organic material that could foul the analytical column. The analytical method included a 9.0 mM sodium carbonate eluent, 1.0 mL/min flowrate, and 250 The typical dissolved organic carbon concentration of CU water is approximately 1.5 µL injection loop. The anions were detected by suppressed conductivity.

Perchlorate Analysis. Perchlorate was analyzed by the same ion chromatography system. However, the columns used were NG 1, AG11, AS11. The limit of detection (LOD) for perchlorate was calculated to be approximately 2.2 µg/L. Any perchlorate concentration that appeared to be lower than the LOD was considered to be at the LOD.

Dissolved Oxygen Analysis. Dissolved oxygen was measured using a YSI Model 58 dissolved oxygen meter with a 5905 probe (Yellow Springs, Ohio).

Ammonia Analysis. Ammonia was measured using an Orion 720A pH/Ion Selective Electrode Meter with an Orion ammonia probe 95-12 (Beverly, Massachusetts).

Results and Discussion

Ion Exchange Capacity

As the GAC filters were acclimating biologically, data were gathered regarding the abiotic removal of perchlorate by the GAC. For the first 1600 bed volumes (BV) of flow through the 25 minute CUW filter, perchlorate was removed. After 1600 BV, perchlorate is leaching off the GAC as evidence by C/Co values greater than 1 for the filter. A mass balance calculation after 5800 BV demonstrated that the entire mass of perchlorate which had been applied to the filter up to that point, had shown up in the effluent of that filter. Therefore, any removal of perchlorate up to that point was the result of sorption, probably ion exchange. To calculate the (probable) ion exchange capacity of the GAC, the area above the curve and below $C/C_o = 1$ from $0 \leq BV \leq 1600$

was integrated. This integration showed an ion exchange capacity of 0.172 mg ClO_4^- (1.7 x 10^{-6} mole) per gram GAC.

Biological Reduction of Perchlorate

After the first 5800 BV, syringe pumps were installed to add an electron donor solution (mixture of acetate, lactate, and pyruvate; 2 mg/L as carbon, 5 mg/L of equivalent oxygen demand) to the influent water at the point of entry to the carbon bed. Table 1 describes the perchlorate removal results for the syringe pump experiments using DDW.

Table1. ClO_4^- Removal in DDW with DO_o=2.5 mg/L and Various NO_3^- Concentrations

#	EBCT	Influent		Effluent			ClO_4^- Removal (%)
		NO_3^- (mg/L)	ClO_4^- (µg/L)	DO (mg/L)	NO_3^- (mg/L)	ClO_4^- (µg/L)	
1	25	4.5	51.0	0.1	2.0	50.0	2
2	25	1.4	52.0	0.1	0.07	2.0	96
3	25	1.4	52.0	0.1	0.30	19.6	62
4	25	2.4	55.0	0.1	0.39	31.8	42
5	25	2.4	55.0	0.1	0.10	10.3	81

It is important to first note that biological removal of perchlorate has been achieved. Ion exchange capacity of the GAC had been exhausted after less than 2000 BV of flow. There was no evidence that perchlorate can be chemically reduced by GAC. Therefore, any removal demonstrated after 2000 BV is the result of biological reduction. The second point of import shown in Figure 3 is that with dissolved oxygen concentrations held low and constant, the biological reduction of perchlorate is highly sensitive to the concentration of nitrate present in the water. As nitrate concentrations increase, perchlorate removal decreases.

Perchlorate removal was also observed in the CUW BAC filter. However, nitrification of influent ammonia reduced control over influent conditions and confounded the data.

Conclusions

In summary, this work has shown that

- Perchlorate is removed abiotically on Norit GAC via ion exchange and not chemical reduction.
- Norit GAC has a relatively low ion exchange capacity for perchlorate.
- Microorganisms present in BAC filters can reduce perchlorate at low µg/L concentrations.

- The biological reduction of perchlorate is highly sensitive to the concentration of nitrate present in solution.

The main significance of this work is that biological reduction of perchlorate in the low µg/L concentration range has been achieved. Though it would be ideal to eliminate the need for an external electron donor solution, achieving removal is the first step to establishing a readily implementable biological treatment process for perchlorate removal.

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